In-situ Solvothermal Synthesis of Novel High-Capacity Cathodes

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2018 Annual Merit Review and Peer Evaluation Meeting (AMR), June 18-21

BAT #183

Overview

Timeline

- Start date: Oct., 2015
- End date: Oct., 2018
- Percent complete: 70%

Barriers

- Barriers addressed
  - Low energy density
  - Cost
  - Cycle life

Budget

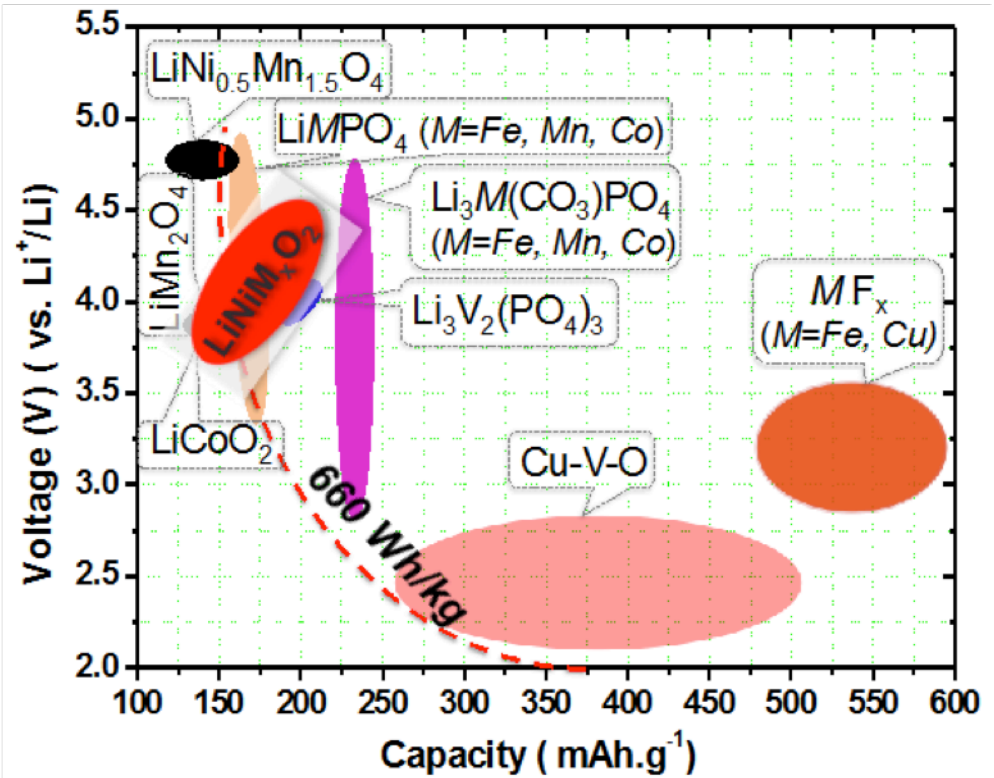
- Total project funding
  - DOE 100%
- Funding received in FY 2017
  - 350K
- Funding received in FY 2018
  - 350 K

Partners

- Interactions/collaborations
  - Lawrence Berkeley National Lab
  - Oak Ridge National Lab
  - Argonne National Lab
  - Stony Brook University
- Project lead
  - Brookhaven National Lab

Relevance and Objectives

Develop low-cost cathode materials with high energy density and electrochemical properties (*cycle life, power density, safety, …*) consistent with USABC goals.



The effort in FY17-FY18 is focused on developing Ni-Mn-Co layered oxides (NMC) based high-Ni cathodes, through *in-situ* probing and synthetic control of the

- phase
- stoichiometry, and
- morphology

of the active materials.

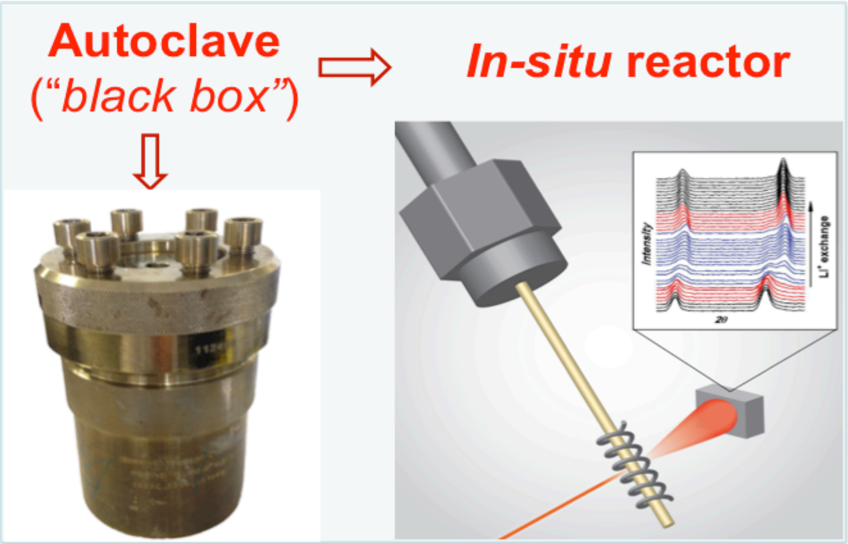
(**Some cathodes with target energy density (>660 Wh/kg) are given on the right side of the red dashed plot*)

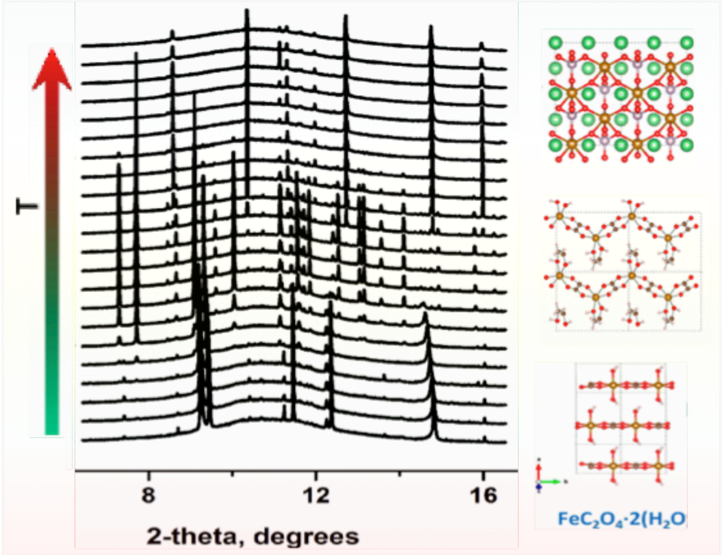
Approach: *Synthesis by Design*

Electrochemical performance of electrodes, which is largely determined by the phase, stoichiometry, morphology of the active materials, can be advanced by

- synthesis of *phase-pure* materials
- control of *stoichiometry*, *morphology*

➢ *In-situ* techniques are developed for structure-tracking aided synthetic design of electrode materials of desired phases and properties

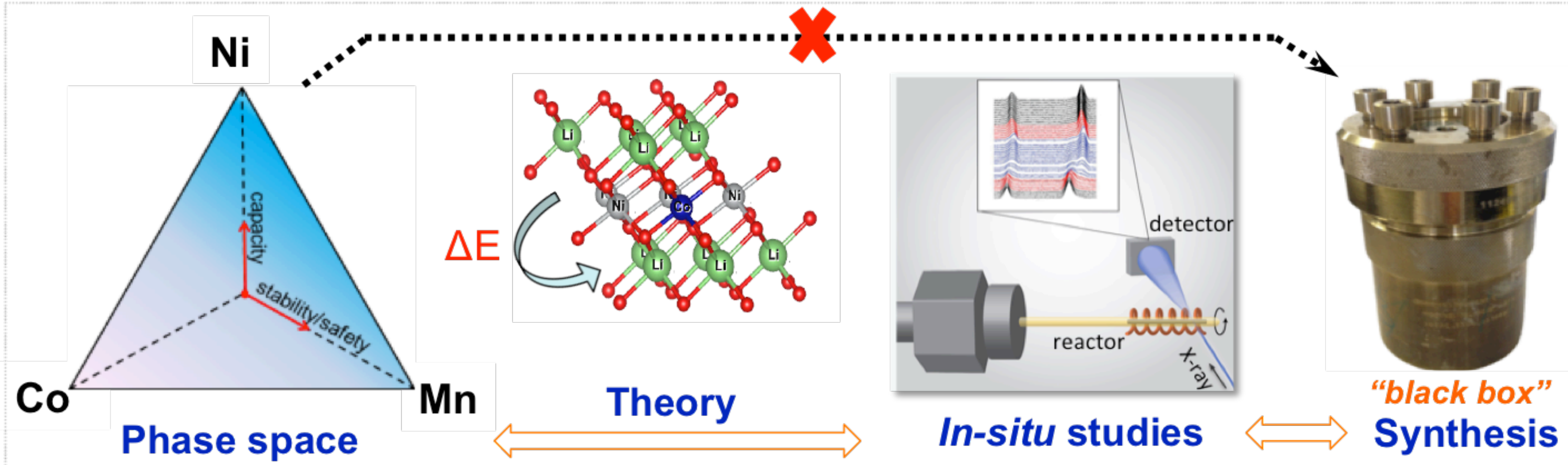




Ref.: Bai *et al.*, J. Phys. Chem. C, 119 (2015) 2266

Approach: ***Synthesis by Design*** *(Ni-rich NMC)*

Ni-rich NMC: cationic disordering/off stoichiometry (**among many other issues*)



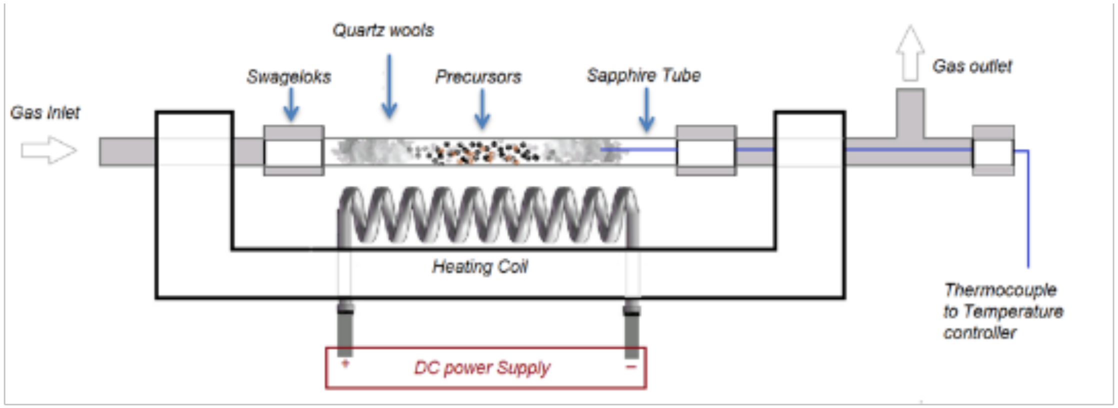
Approach: synthetic design via *in-situ* probing synthesis reaction

- explore "phase space" under the real, often *non-equilibrium* synthesis conditions
- track phases/cationic ordering in the intermediates *and, thereby,* quantify thermodynamic/kinetic parameters governing the synthesis process.

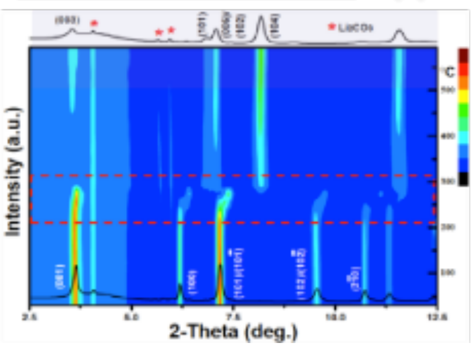
Milestones

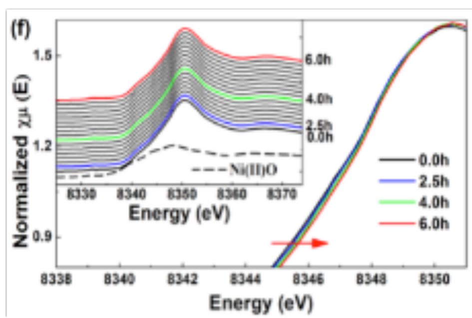
Time	**Description (*status*)**
June, 2017	Identify synthesis procedures for kinetic control of structural ordering in NMC layered oxides through combined *in-situ*/*ex-situ* synchrotron X-ray and neutron studies.(*complete*)
Sept., 2017	Complete the evaluation of synthesis conditions, and identify the effect of temperature and time on the structural ordering, electrode performance of Ni-rich NMC layered cathodes. (*complete*)
Dec., 2017	Develop spatially resolved *in-situ* techniques for probing local oxidation and ordering of cations in NMC layered oxides during synthesis at high temperatures. (*complete*)
March, 2018	Identify the roles of Mn/Co substitution in tuning Li/Ni mixing in high-Ni NMC layered oxides. (*delayed*)
June, 2018	Develop procedures for synthetic control of structural ordering in compositionally heterogeneous NMC oxides. (*pending*)

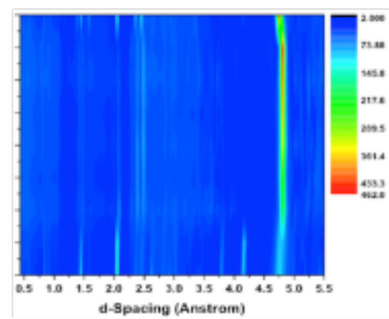
Accomplishment (1) Developed *in-situ* techniques, allowing for multimodal characterization of solid-state synthesis under controlled atmosphere

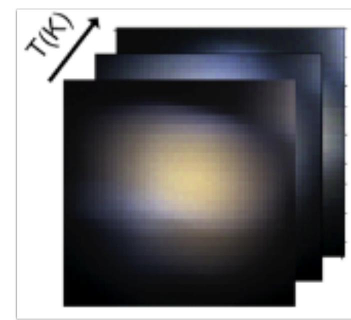


X-ray scattering | X-ray absorption | Neutron scattering | Spectro-imaging



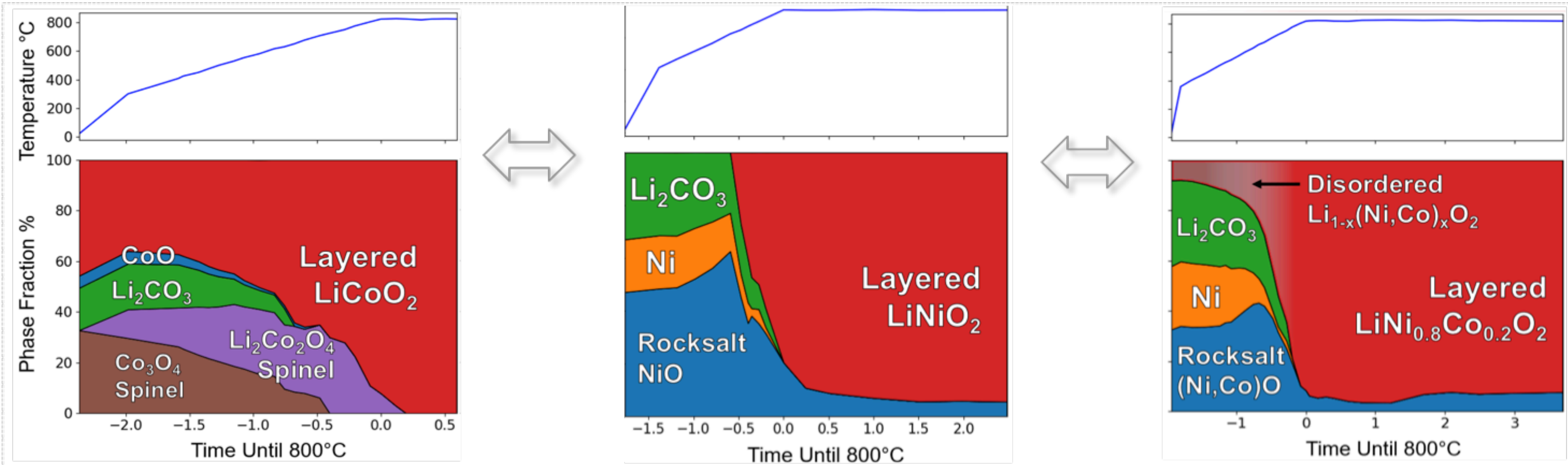


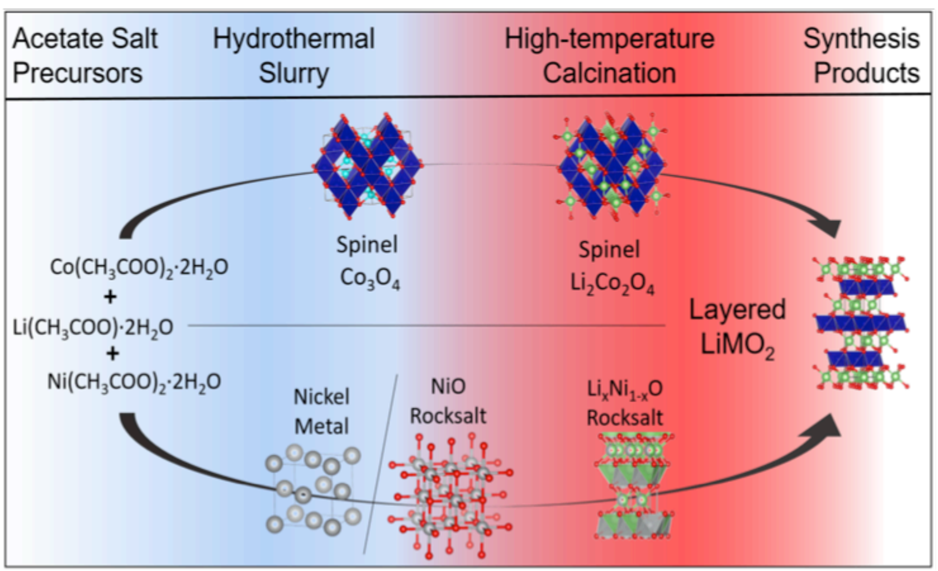




- Development of *in-situ* reactors/techniques provides allows for probing the kinetic process of local cationic inter-diffusion and ordering in Ni-rich NMC layered oxides as they are being synthesized.

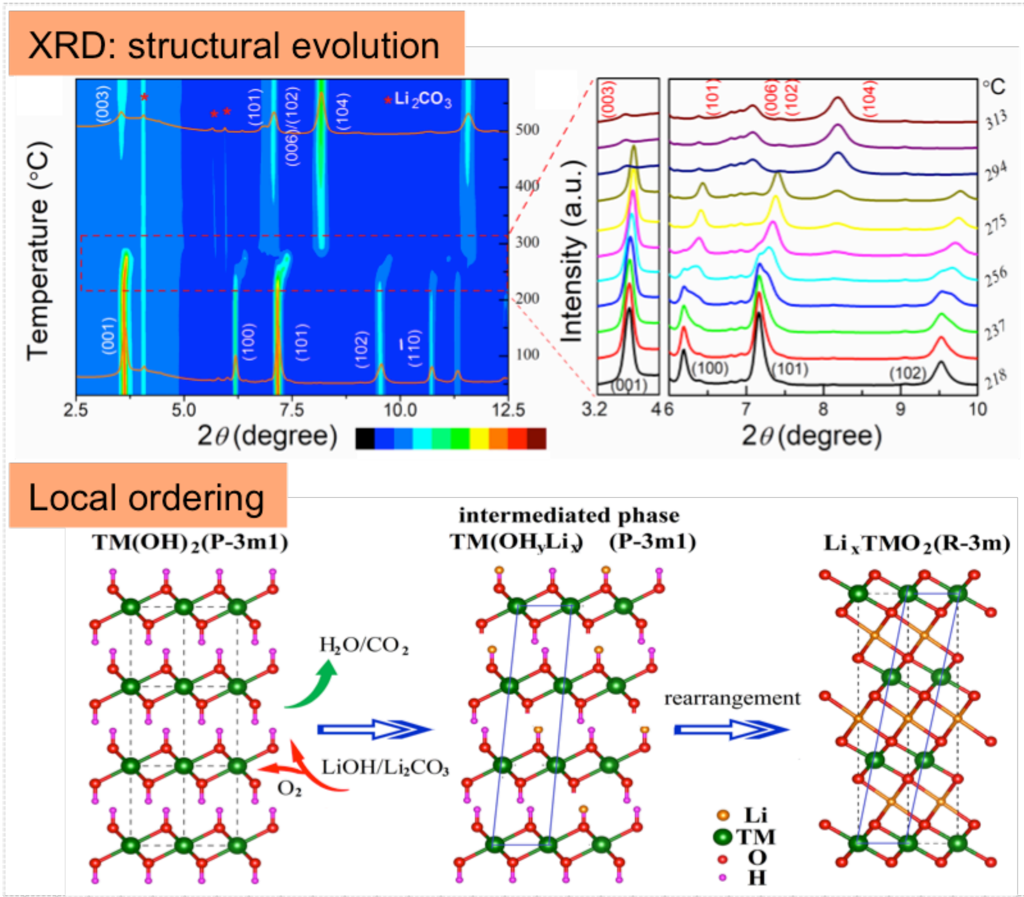
Accomplishment (2) Identified the role of precursors in governing pathways during synthesis of Ni/Co-based layered oxides

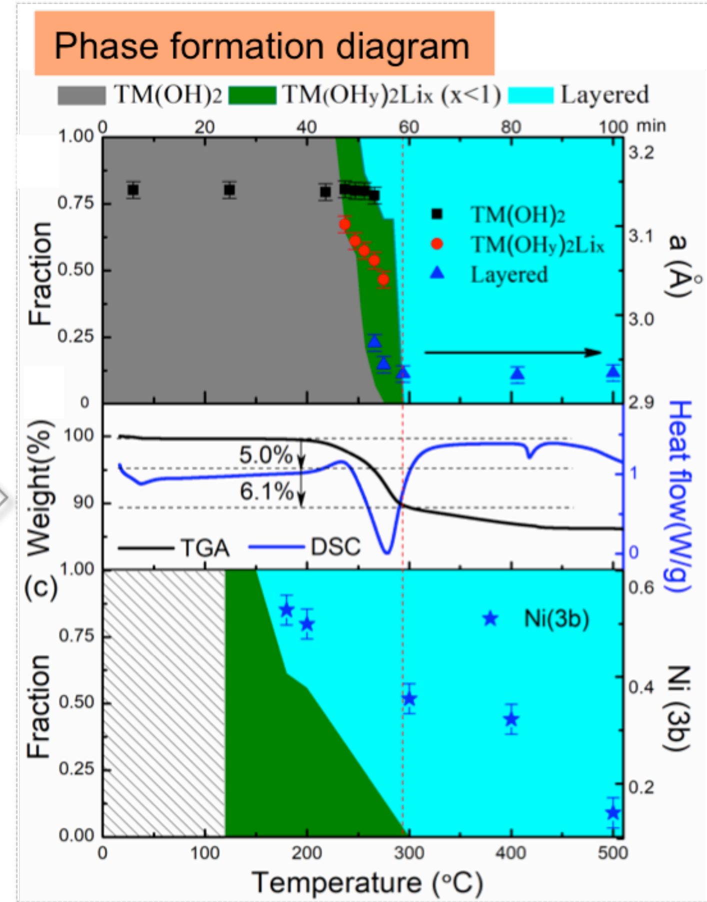




- **$LiCoO_2$**: Co- acetate precursor first oxidizes to Co_3O_4, and then turns into topotactically-related $Li_2Co_2O_4$
- **$LiNiO_2$**: goes directly from rock-salt intermediate to the layered phase
- **$LiNiCoO_2$**: similar to $LiNiO_2$, but goes through a *disordered* rock-salt ➔ control of the pathways *via* manipulating precursors

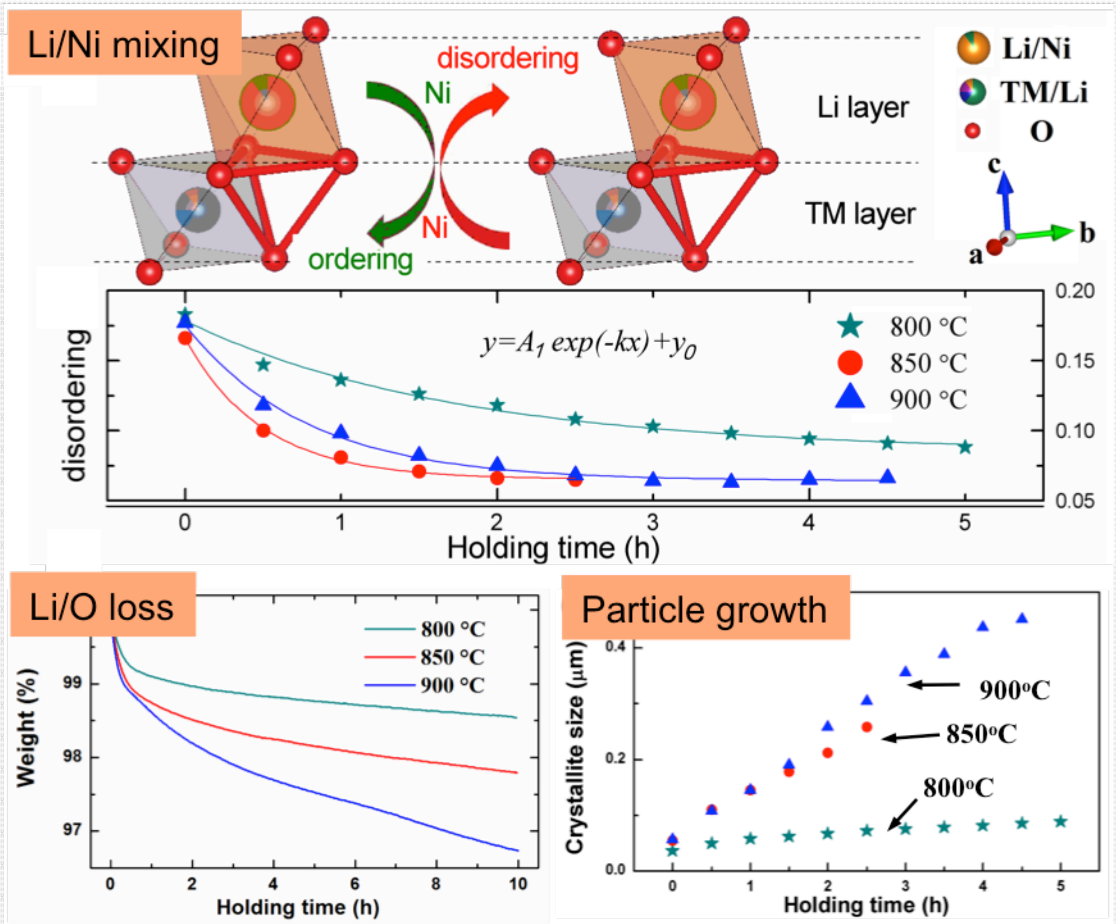
Accomplishment (3a) Identified the kinetic reaction pathway in synthesis of $LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2$ (NMC71515) from hydroxides

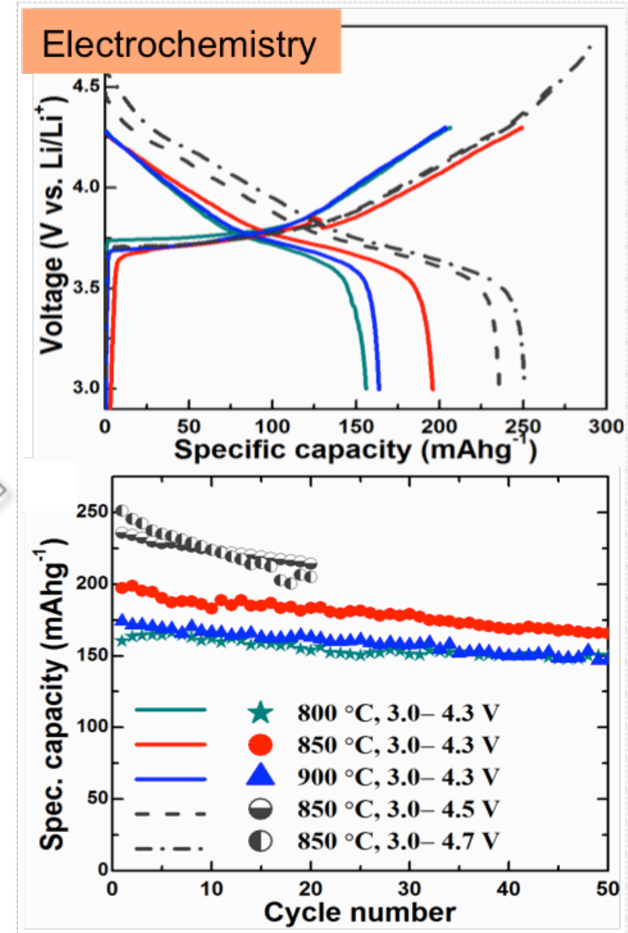




- Formation of layered phase at low temperatures
  - involving intermediates, wherein the O-framework is overall retained; while inter-layer gliding occurs: *hcp*➔ *ccp*
  - crucial role of Mn/Co substitution in facilitating transition to the layered structure

Accomplishment (3b) Identified synthesis procedures for kinetic control of the structural ordering in NMC71515

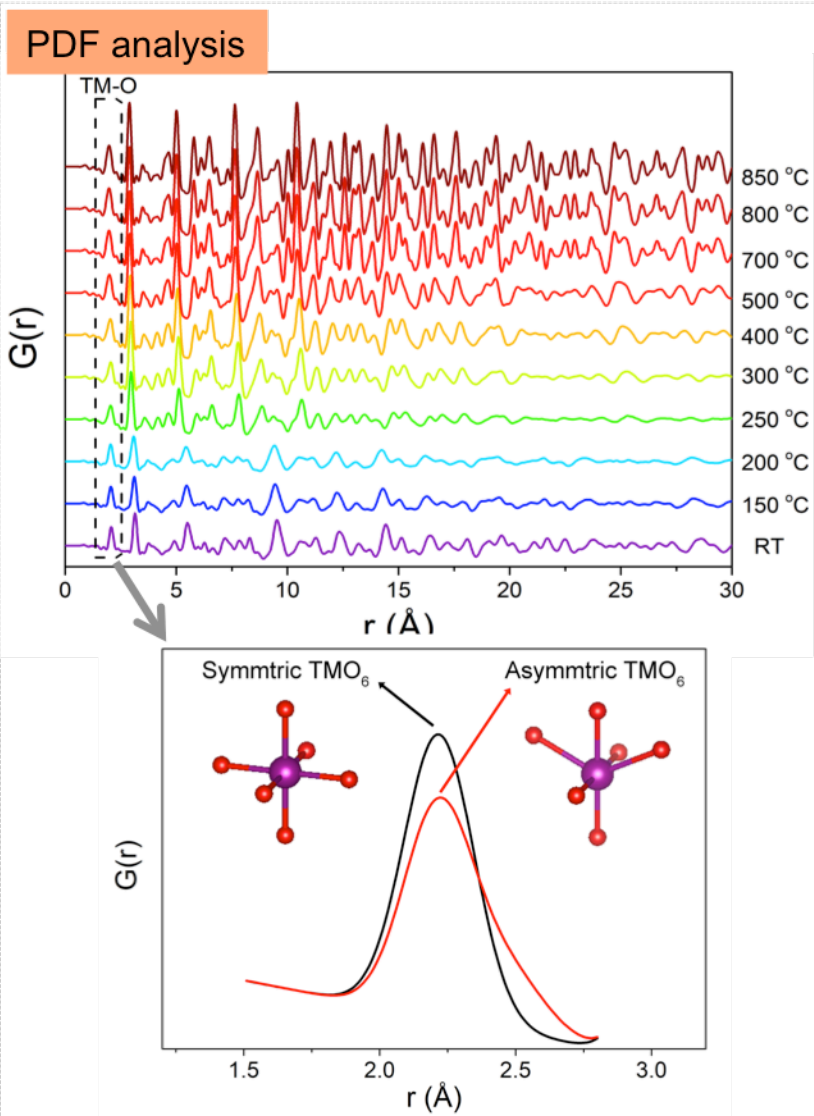


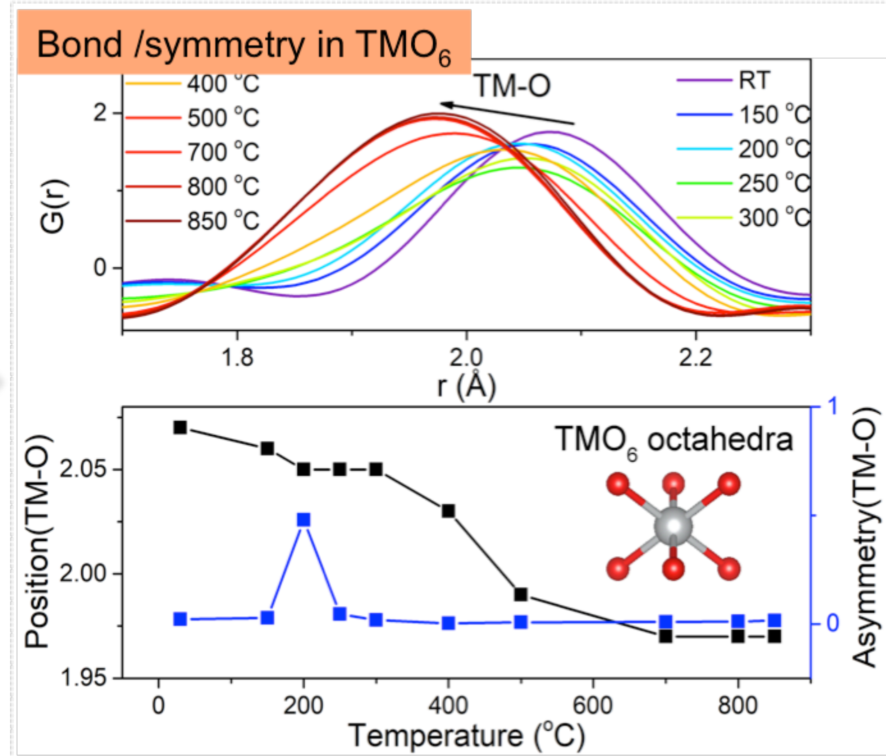


- Strong temperature dependence of the kinetics of structural ordering
  - thermal-driven cationic ordering/disordering due to Li/O loss
  - kinetic control of cationic ordering/morphology, thereby optimizing performance

Ref.: Wang et al., Adv. Mater., 29 (*2017*) 1606715

Accomplishment (3c) Identified local symmetry evolution of the basic building units (BBUs; *e.g.*, TMO_6) *via* X-ray total scattering

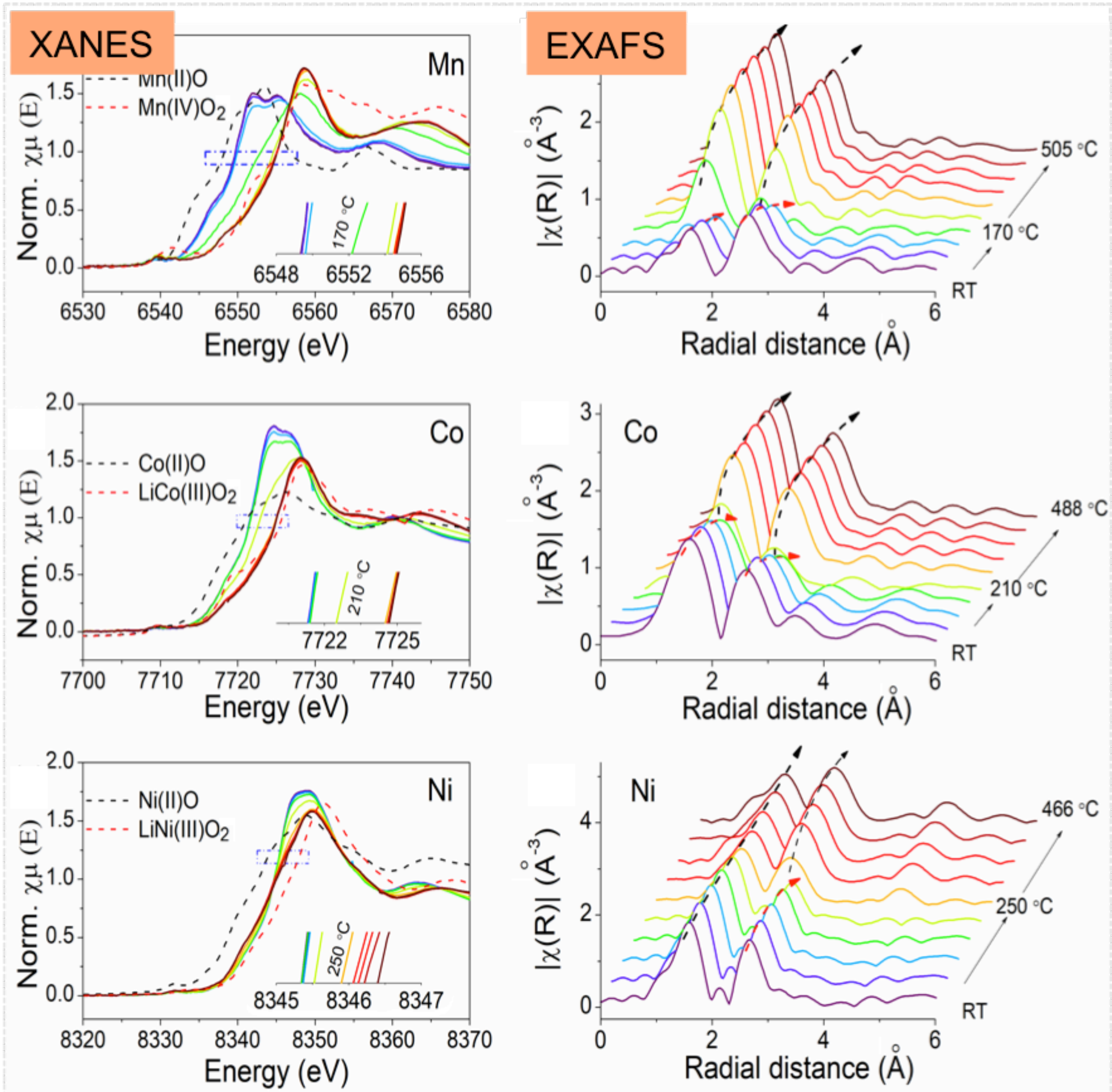


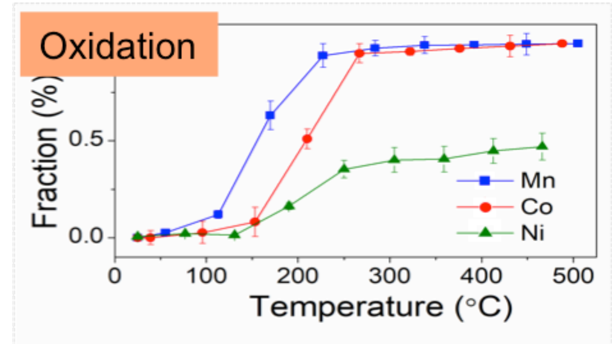


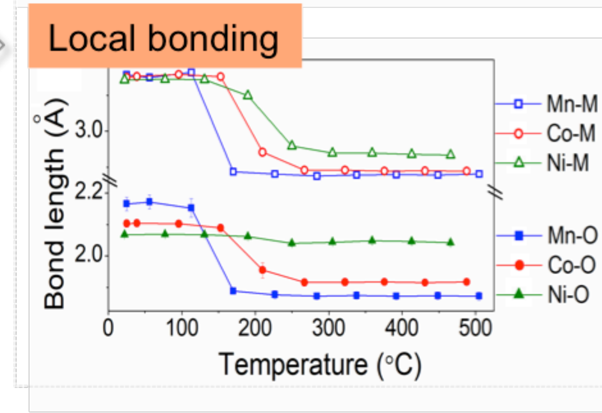
- Developed PDF-based techniques for probing local structural change
  - position of the TM-O peak: bond length
  - shape of the peak: symmetry of TMO_6

    ➔ local symmetry breaking occurred at ~ 200 °C during oxidation of TMs

Accomplishment (3d) Identified oxidation process of all the constituent transition metals (*Ni, Co, Mn*)

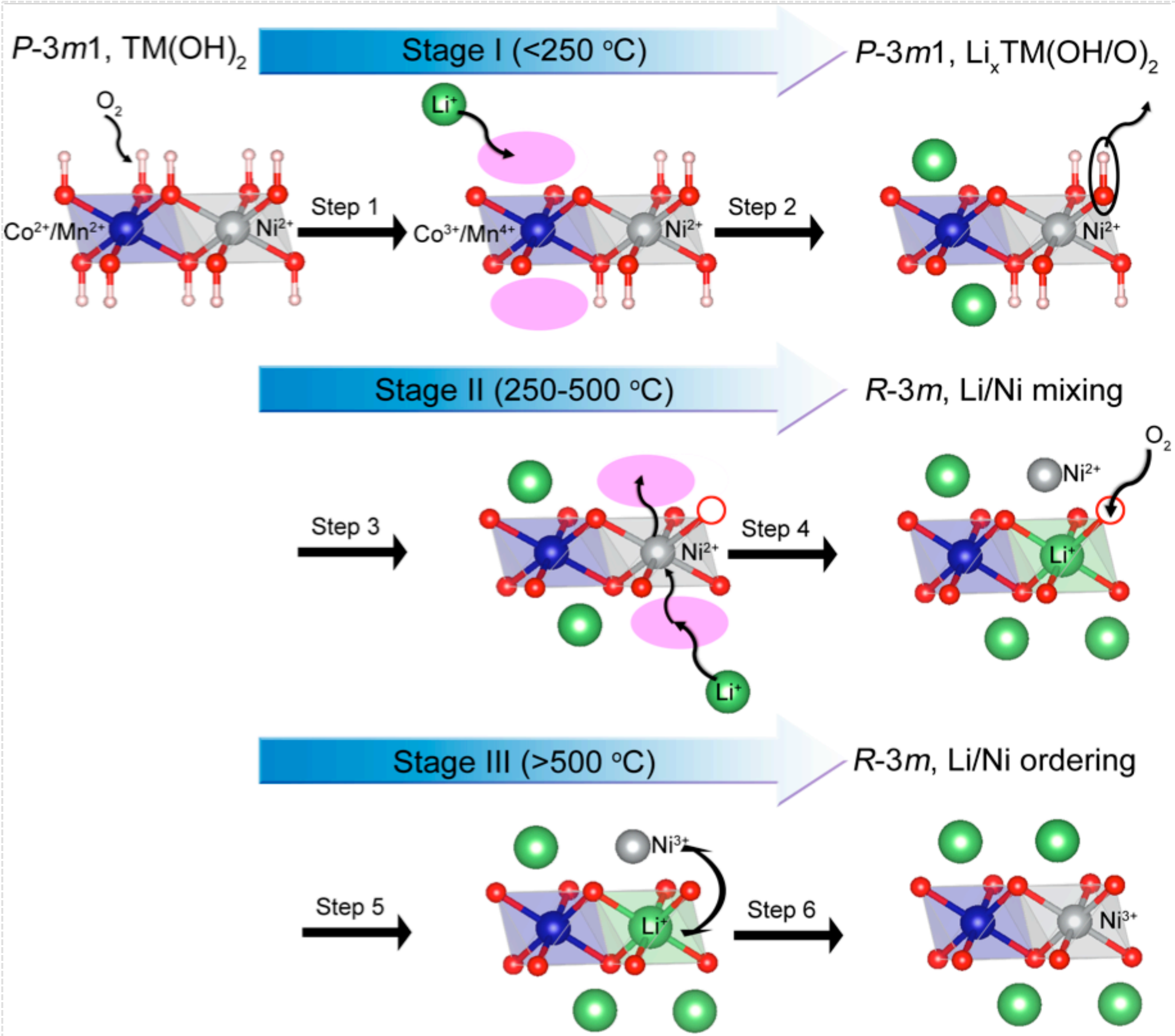






- Preferential oxidation of Mn/ Co over Ni
  - full oxidation of Mn/CO at low temperatures (< 250 °C)
  - slow oxidation in Ni during the whole heating process.

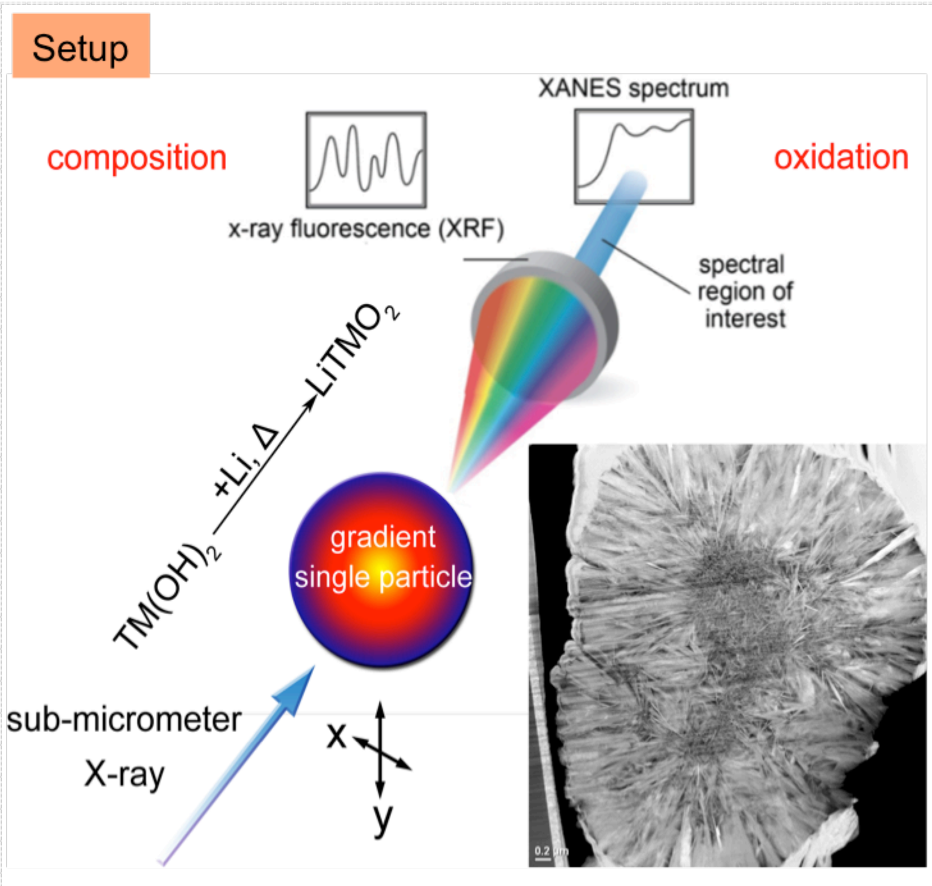
Accomplishment (3e) Reaction pathway during preparing NMC71515 from hydroxide precursors: summary

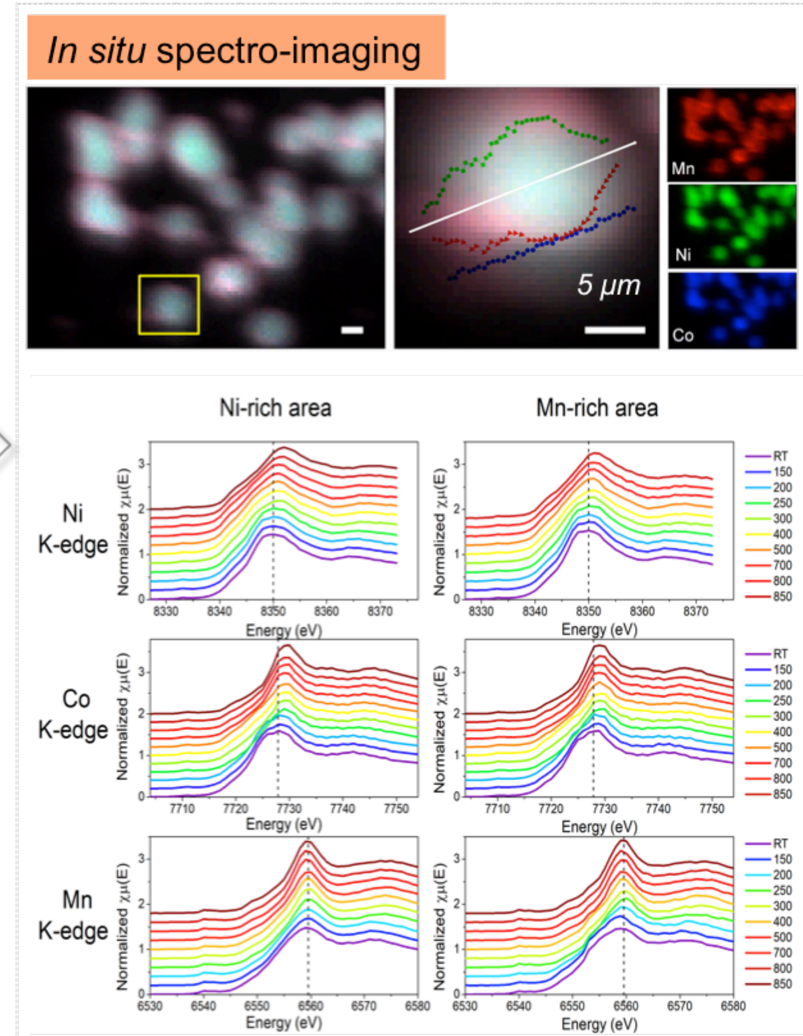


- Preferential oxidation of Mn and Co over Ni:
  - a pre-requisite for retaining the layered framework
- Symmetry breaking/ reconstruction of NiO_6
  - high diffusivity of Ni
  - ➔ *Li/Ni mixing*
- Li/Ni ordering, governed by slow Ni oxidation

- Guidance to synthetic design of high-Ni NMC with low cationic disordering

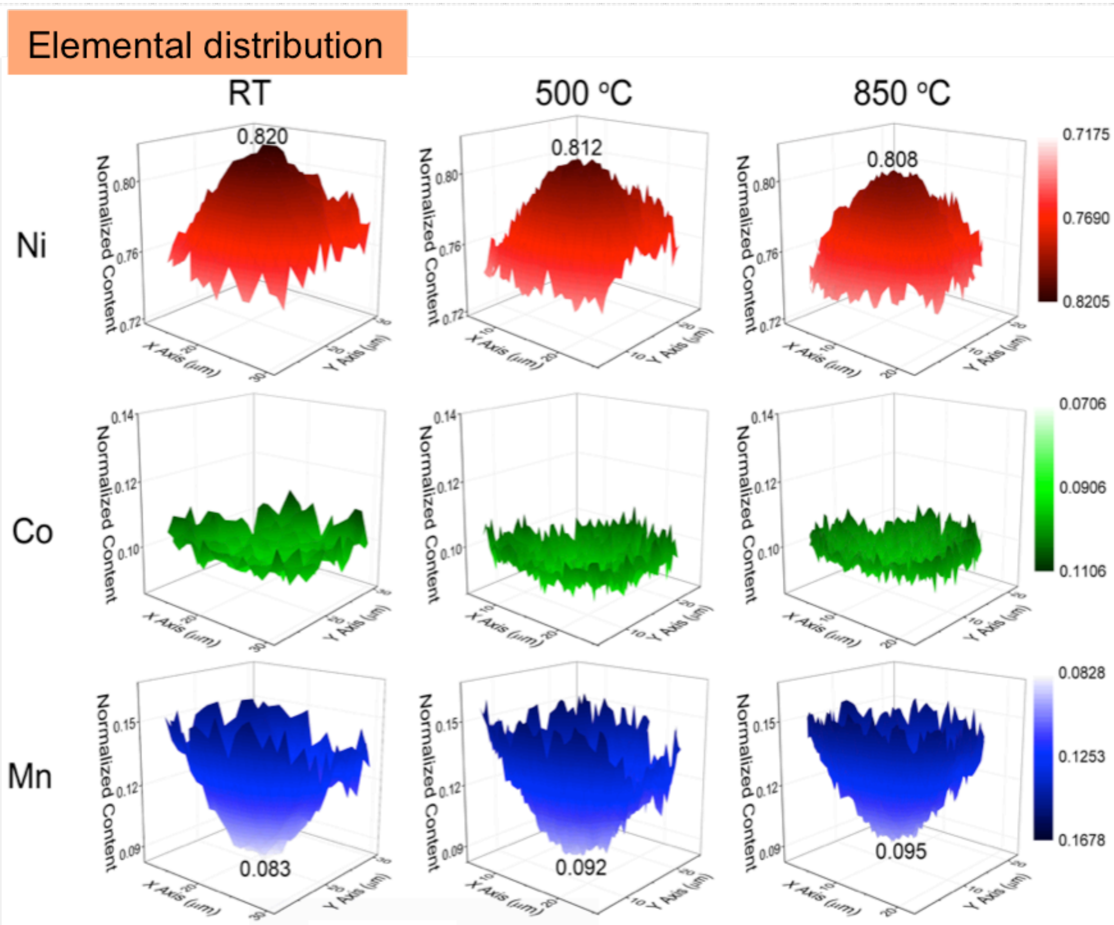
Accomplishment (4a) Established spatially resolved *in-situ* techniques for probing local oxidation/ordering within individual particles during synthesis

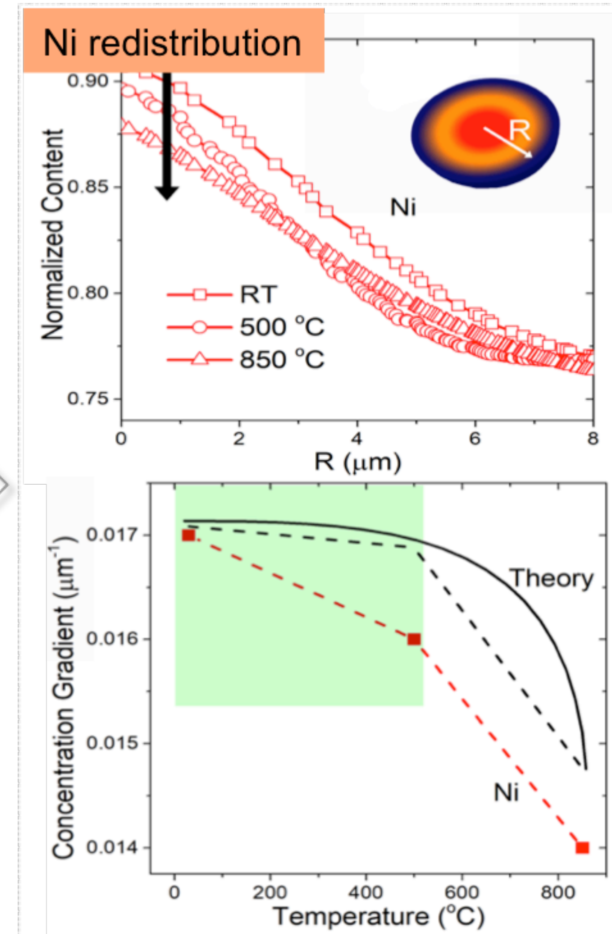




✧ Schematic illustration of the Setup for multimodal *in-situ* X-ray spectro-imaging of a single particle during high temperature synthesis

Accomplishment (4b) Identified cationic inter-diffusion within individual concentration gradient particles during synthesis





- Elemental distribution/inter-diffusion within a single particle was quantified
  - unexpected fast Ni/Mn inter-diffusion below 500 °C, comparable to that at high temperatures

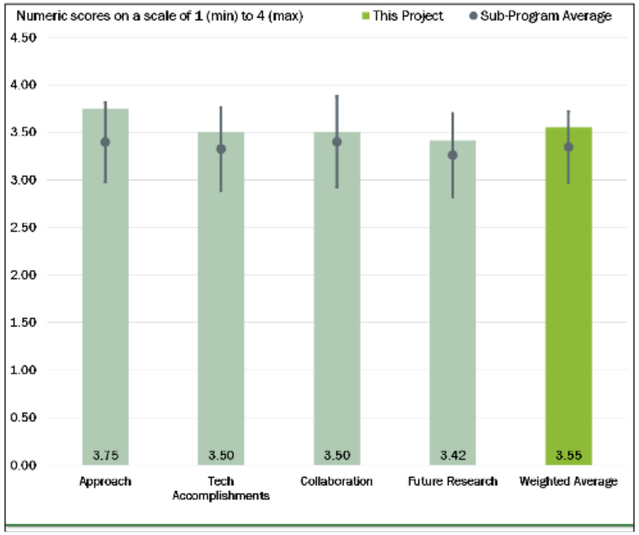
Response to Reviewers' Comments

We thank the reviewers for their comments. Most of them are positive, and so we only provide response to several comments/suggestions below.

1. " The reviewer stated that it would be great to extend this to other synthesis methods — even if they had to be *ex situ* with sampling of materials as a function of time. It needs to include commercially relevant processes*."*

-- In FY18, we have re-focused our studies on solid-state synthesis using hydroxide precursors, which, we think, is more commercially relevant;

-- We have also initialized collaboration W/ the MERF facility at Argonne on studying material synthesis in large scale, using commercially relevant processes.



2. "The reviewer gained great insights concerning the local and long range structures of transition metals in NMC family materials but would like to have seen some correlations between these synthetic variations and stability over cycles and more detail about the capacities."

-- We have made extensive electrochemical tests of the synthesized materials and indeed identified close correlation between the synthesis conditions and electrochemical performance (capacities, cyclability, …). Those results have been included in the report or submitted for publication.

Response to Reviewers' Comments *(continued)*

3. "The reviewer highly recommended that efforts continue to advance this year's work and develop new *in-situ* techniques for thorough mapping of synthetic parameters and resulting structure and electrochemical properties. Close collaboration with other BMR projects on materials development should be done."
-- New *in-situ* techniques for multimodal characterization were developed in FY18, as included in this report;
-- A large portion of this research project was done through collaboration with PIs in the BMR program. We have also initialized new collaborations on developing different types of materials.

4. "The reviewer commented that it will also be important to study the effect of Mn in the high-Ni NMC materials and compare that to the NCA materials with the similar Ni content."
-- Some studies have been done on the Mn effect in a series of high-Ni layered oxides. We also initialized studies on NMC811 (with similar Ni content to NCA).

5. "Some concerns on the limited beam time "the practical limitations on beam time may impede this project."
-- We actually got more than enough beam time in FY17, both for this project and for collaborations;
-- We have secured significant beam time for FY18, and expect to get more beam time in the upcoming FY19 as new beamlines in NSLS-II come online.

Collaborations

- **Brookhaven National Lab** (*J.P. Looney, L. Wu, Y. Zhu, K. Chen*)
  - *Techniques/capabilities for synthesis and characterization of new cathodes*
  - *Advanced TEM imaging and spectroscopy of cathodes*
- **Argonne National Lab** (*Z. Chen, Y. Ren, C. Sun, K. Amine, Y-H. Shin, G. Krumdick*)
  - *Synthesis and characterization of Ni-rich layered cathodes*
  - *Characterization of the battery materials from scale-up facility (MERF)*
- **Lawrence Berkeley National Lab** (*W. Sun, G. Ceder, N. Balsara, W. Tong*)
  - Theoretical prediction of the phases/ordering in Ni-rich layered cathodes
  - Synthesis and characterization of cathode materials
- **Oak Ridge National Lab** (*J. Nanda, A. Huq*)
  - *Neutron/synchrotron characterization of Ni-rich layered cathodes*
- **Xiamen U.** (*Y. Yang*)
  - *Characterization of layered cathodes for working at high voltages*
  - *Develop high-voltage polyanionic cathodes*
- **Alfred U.** (*S. Misture*)
  - *In-situ synthesis and characterization of Ni-rich layered cathodes*
- **Stony Brook U.** (*E. Takeuchi, P. Khalifah*)
  - *Synthesis of new high-capacity cathodes*
- **Seoul Nat. U.** (*K. Kang*)
  - *Synthesis/characterization of new high-capacity cathodes*

Remaining Challenges and Barriers

- **Main barrier:** general principles have been established for designing cathode materials, but so far there has been no theory or design principles on synthesizing materials of desired structure/properties: *we know what we want but don't know how to make them.*
- **Technical challenge**: designing and synthesizing specific cathode materials has proven difficult due to the complexity of the reactions involved in chemical synthesis, and high sensitivity of the phases, stoichiometry and morphology to the synthetic parameters (such as *pH value*, *Li content*, *sintering temperature/ atmosphere*, *heating/cooling rates*…)
  - Synthesis of high-Ni layered oxides is even more challenging, due to the demanding requirement on the synthetic control of the cationic disordering and surface rock-salt layer (*both being detrimental to their electrochemical performance*).

Future/On-going Work (*FY18-19*)

- Continue working on *in-situ* structure-tracking aided synthetic design of Ni-rich NMC cathodes, with focuses on
  - impact of cooling-rate on cationic ordering and electrochemical properties (**see preliminary results in Backup Slide 1*)
  - role of Mn/Co substitution on cationic ordering (**Backup Slide 2*)
  - local cationic inter-diffusion/disordering in individual particles with compositional concentration gradient or core-shell configuration
- Develop new *in-situ* techniques/capabilities, specialized for probing synthesis under realistic conditions
  - new techniques for multimodal characterization (*e.g.*, simultaneous or combined X-ay scattering/spectroscopy/imaging) in one-pot synthesis
  - new techniques capable of high spatial resolution and/or high sensitivity to local structural ordering
- Apply the established approaches/techniques to synthesis of different types of electrodes/solid electrolytes for Li-ion, Na-ion and solid-state batteries

Any proposed future work is subject to change based on funding levels

Summary

We have established approaches for structure-tracking aided synthetic design of electrode materials with desired phases, stoichiometry and morphology.

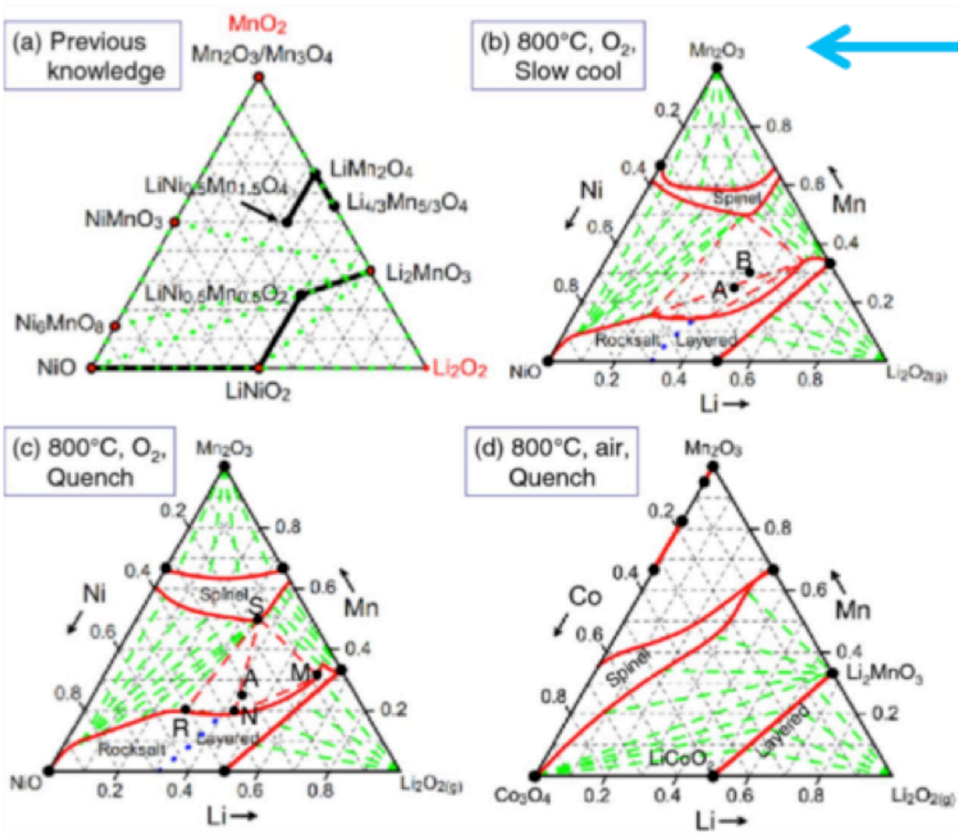
- **Relevance:** Develop synthetic approaches for preparing low-cost, high energy density cathodes with potential application in electric vehicles.
- **Approaches:** *in-situ* techniques/capabilities are developed for probing synthesis reaction in preparation of cathode materials, allowing us to
  - identify reaction pathways/intermediates
  - quantify thermodynamic and kinetic parameters governing synthesis process.
- **Technical Accomplishments:** Synthesis procedures were developed for making a series of high-Ni layered oxides with demonstrated high reversible capacity.
- **Collaborative Research:** Established extensive collaborations within BMR and W/ external partners on synthesis/characterization of cathodes.
- **Future Work:** Apply the established approaches/techniques to synthesis of high-Ni layered oxide cathodes and other type of battery materials.

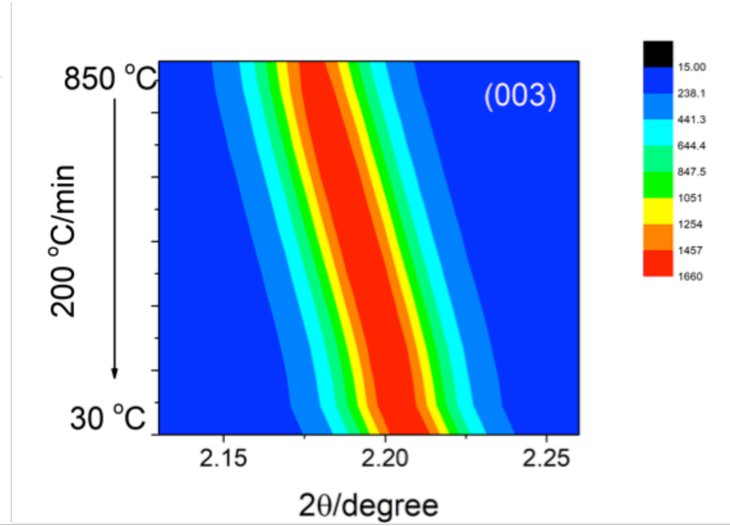
Acknowledgement

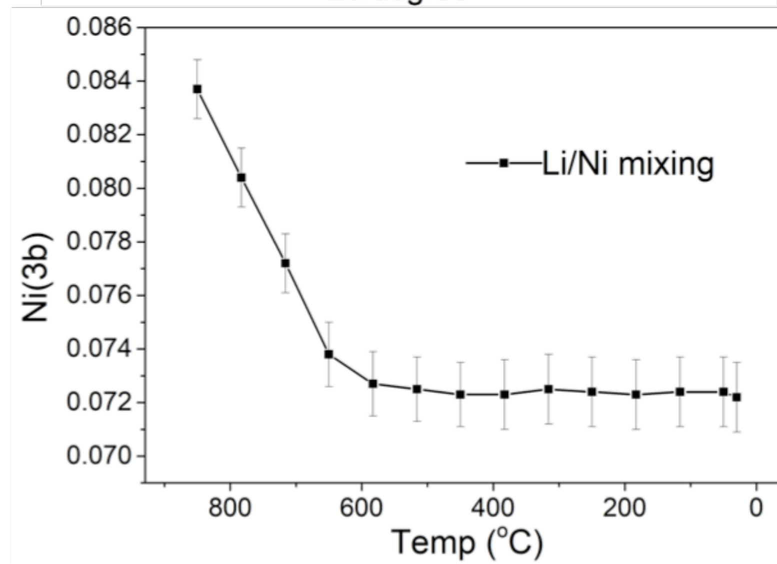
- Support from the BMR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged
- Team members: Mingjian Zhang, J. Patrick Looney

Technical Backup Slides

(1) Preliminary studies of the impact of cooling-rate on: i) phase diagram; ii) structural ordering (➔ electrochemical properties)



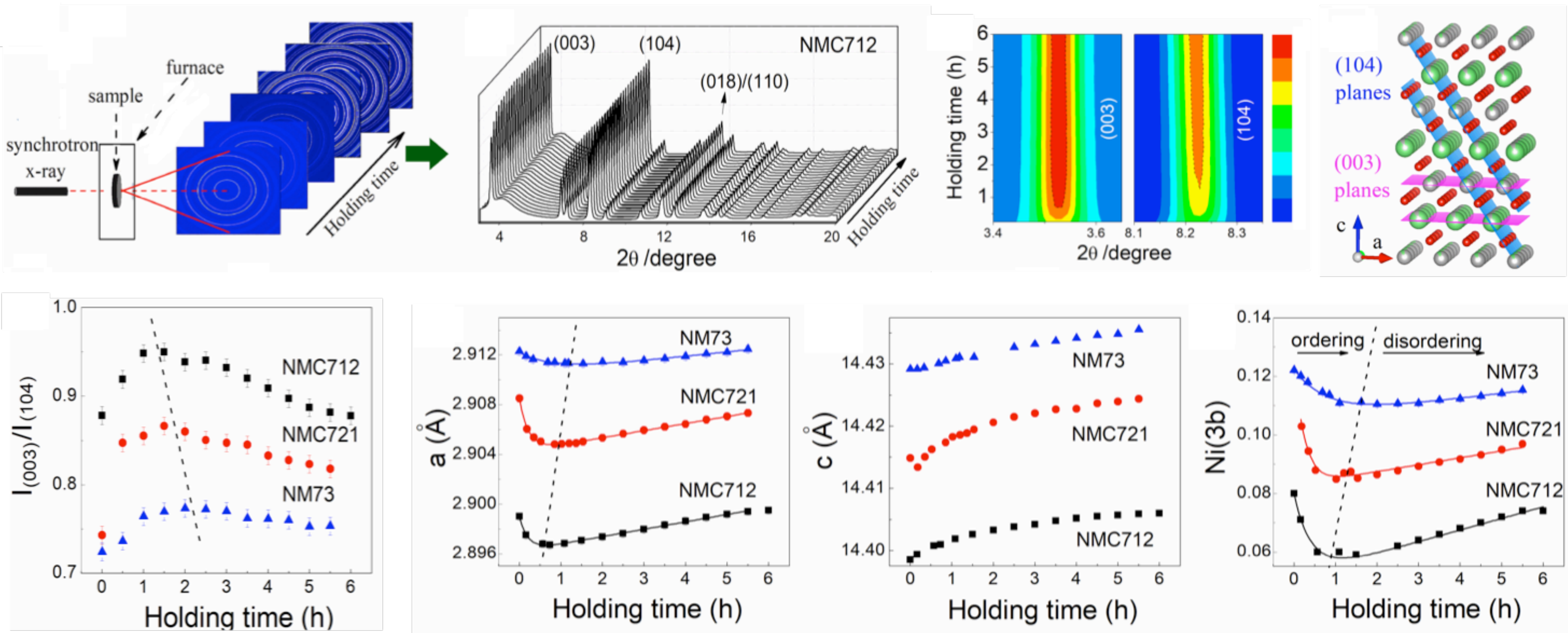




- Strong dependence of the phases Li-Mn-Ni(Co)-O on cooling conditions *(Dahn et al., JES. 160, A1134 (2013))*

➔ ***In-situ* studies:** tracking phase evolution & Li/Ni mixing during cooling

(2) Preliminary studies on the role of Mn/Co substitution in governing the cationic ordering in high-Ni layered oxides



- Kinetics/thermodynamics of structural ordering is quantitatively determined in a series of Mn/Co substituted Ni-rich layered oxides, indicating that:
  - Co substitution facilitates cationic ordering
  - Mn aggravates Li/Ni mixing and slows down the ordering process